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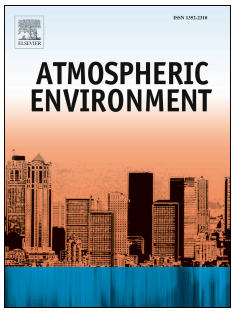

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Oxidative Potential of Subway $PM_{2.5}$

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ABSTRACT

Air quality in subway systems is of interest not only because particulate matter (PM) concentrations can be high, but also because of the peculiarly metalliferous chemical character of the particles, most of which differ radically from those of outdoor ambient air. We report on the oxidative potential (OP) of $PM_{2.5}$ samples collected in the Barcelona subway system in different types of stations. The PM chemical composition of these samples showed typically high concentrations of Fe, Total Carbon, Ba, Cu, Mn, Zn and Cr sourced from rail tracks, wheels, catenaries, brake pads and pantographs. Two toxicological indicators of oxidative activity, ascorbic acid (AA) oxidation (expressed as OP^{AA} μg^{-1} or OP^{AA} m^{-3}) and glutathione (GSH) oxidation (expressed as OP^{GSH} μg^{-1} or OP^{GSH} m^{-3}), showed low OP for all samples (compared with outdoor air) but considerable variation between stations (0.9-2.4 OP^{AA} μg^{-1}; 0.4-1.9 OP^{GSH} μg^{-1}). Results indicate that subway PM toxicity is not related to variations in $PM_{2.5}$ concentrations produced by ventilation changes, tunnel works, or station design, but may be affected more by the presence of metallic trace elements such as Cu, As and Sb sourced from brakes and pantographs. The OP assays employed do not reveal toxic effects from the highly ferruginous component present in subway dust.

Keywords: particulate matter, oxidative potential, toxicity, PM chemistry, subway air quality, airborne metals.

Highlights

- Oxidative activity shows considerable variation between different subway platforms
- Subway PM oxidative potential is not linked to ventilation or tunnel night works
- Highest oxidative potential coincide with PM with higher levels of Cu, As and Sb
- The strongly Fe component in PM subway does not produce any obvious toxic effect
- Lowest oxidative stress was found at station with PSDs

1. Introduction

Over 160 million passengers travel daily in the 156 subway systems around the world, representing around 11% of public transport journeys worldwide, and these numbers are increasing. In the last year alone the subways of Beijing and Shanghai have recorded an increase of 39% and 25% respectively over the previous year (UITP, 2015), making it clear that this form of transport will play an ever-greater role in future megacity commuter mobility. While mass transport of commuters by subway train is to be strongly encouraged over the use of road traffic, one possible area of concern is the quality of air breathed while underground in trains and on station platforms because inhalable particulate matter (PM) levels can be higher than those above ground. Many published studies in subway systems worldwide have reported average platform PM_{10} concentrations that exceed 50 μg m^{-3}, and in some cases 300 μg m^{-3} (Fromme et al., 1998; Johansson and Johansson, 2003; Seaton et al., 2005; Braniš, 2006; Ripanucci et al., 2006; Salma et al., 2007; Kim et al., 2008; Park and Ha, 2008; Raut et al., 2009; Ye et al., 2010; Cheng and Yan, 2011; Kam et al., 2011a; Querol et al., 2012; Colombi et al., 2013). Subway PM is mainly generated by the mechanical abrasion of rail/wheel and brakes, from the catenary (overhead line equipment) and the resuspension of material caused by air turbulence in the stations and tunnels. Thus, the air quality of a given subway platform will depend on a complex interplay of factors such as the ventilation system, train speed and frequency, wheel materials and braking mechanisms, and station depth and design (Moreno et al., 2014 and references therein).

Numerous studies have shown negative health effects related to exposure to ambient PM_{10} or $PM_{2.5}$ mass concentrations (e.g. Brunekreef and Holgate, 2002; Pope and Dockery, 2006). However, in this context considering mass concentration alone is not necessarily enough because it ignores sources, constituents, and biologic activity of the PM (Ayres et al., 2008), so that current knowledge does not allow precise quantification of the health effects of individual PM components or of different PM sources (Brunekreef, 2010; WHO, 2007). The capacity of inhaled particles to generate reactive oxygen species (ROS), or free radicals, at the air–lung interface has been suggested to trigger

oxidative stress, leading to adverse health effects (Kelly, 2003; Pourazar et al., 2005). The oxidative potential (OP), defined as a measure of the capacity of PM to oxidize target molecules, has been proposed as a measure that is more closely related to biological responses to PM exposure and thus could be more informative than PM mass alone as it integrates various biologically relevant properties, including size, surface and chemical PM composition (Borm et al., 2007). There are a number of methods suggested for measuring OP, but no consensus has been reached yet as to which assay is most appropriate as they seem to be affected differently by different PM characteristics (Ayres et al., 2008; Janseen et al., 2014).

The effects of metallic subway particles on oxidative stress and ROS activity in alveolar macrophage cells have been considered in several published studies, in relationship to PM shape, size, surface area and/or chemical constituents (Steenhof et al., 2011; Jung et al., 2012), but the results show little clarity on whether subway PM is relatively more toxic than outdoor PM highly influenced by road traffic-generated particles. Thus, whereas some studies indicate higher subway OP values (Janseen et al., 2014), ROS activity (Kam et al., 2011b) or genotoxicity (Karlsson et al., 2005) compared to outdoor PM samples, comparisons with samples of magnetite, hematite, Cu and Cu–Zn failed to produce the same toxic response. Moreover, in one study particles from street level appeared to be actually more potent in inducing generation and release of inflammatory cytokines (Karlsson et al., 2008a). A recent study by Spagnolo et al. (2015) failed to detect higher levels of cytotoxicity or oxidative stress in the subway system compared with street PM, supporting an earlier conclusion by Seaton et al. (2005) that "those principally at risk from dust inhalation by working or travelling in the London Underground should not be seriously concerned, although efforts to reduce dust concentrations should continue, since the dust is not without toxicity". Grass et al. (2010) found no dose-response relationship between metal concentrations in $PM_{2.5}$ and biological markers measured in blood and urine samples from New York subway workers. Similarly, and with regard to epidemiological evidence, Gustavsson et al. (2008) concluded that no increased lung cancer risk was found amongst subway train drivers, and so their study did not support the hypothesis that subway particles are more potent in inducing lung cancer than particles in ambient air.

It seems clear that further data are needed to clarify the toxic effects of inhalable subway particles, and with this in mind we present new information on the OP of $PM_{2.5}$ samples collected in the Barcelona subway system, where intensive research campaigns have been carried out under the IMPROVE-LIFE project (http://improve-life.eu/en/) to elucidate PM concentrations, chemistry, sources and controls (Querol et al., 2012; Moreno et al., 2014, 2015; Martins et al., 2015, 2016a, b). For this study the oxidative potential of PM was determined using the validated respiratory tract-lining fluid (RTLF) model (Zielinski et al., 1999; Mudway et al., 2004) that measures the degree to which PM can oxidise three antioxidants commonly found at the surface of the lung, ascorbate (AA),

urate (UA) and reduced glutathione (GSH). This model has already been used to demonstrate the oxidative potential of PM collected at roadside sites, in relationship with increased concentrations of bioavailable metals, predominantly Fe and Cu (Künzli et al., 2006; Kelly et al., 2011).

2. Methodology

2.1. $PM_{2.5}$ collection and analysis

$PM_{2.5}$ samples from six different platforms in the Barcelona subway system were selected for this study. All trains operate electrically (through a catenary) and run from 5 a.m. until midnight every day, with additional services on Friday and Saturday nights and with a frequency between 2 and 15 min, depending on the day (weekend or weekday) and time of day. Night maintenance works involving diesel vehicles or rail maintenance operations are occasional but can have an impact on the platform air quality. The braking system is electric when approaching the platform, changing to non-asbestos pneumatic braking when slowing down below a 5 km h^{-1} velocity for all lines using either frontal or lateral brake pads.

A high volume sampler (HVS, Model CAV-A/MSb, MCV) with a $PM_{2.5}$ head was equipped with quartz microfiber filters and programmed to sample $PM_{2.5}$ over 19 h (from 5 a.m. to 12 p.m., subway operating hours) at a sampling flow rate of 30 m^3 h^{-1}. The equipment was located at the end of the platform corresponding to the entrance point of the train into the station, with no exit access to minimise the complexity of air turbulence and annoyance to passengers. A field blank was taken at each station where sampling was done during 30 consecutive days in summer and winter conditions for comparison, as the ventilation system in the subway operates at different settings, being stronger in summer. Three representative $PM_{2.5}$ samples were selected per campaign, this resulting in 6 samples per station, with a total of 36 samples plus 5 field blanks. $PM_{2.5}$ concentrations were determined gravimetrically using a microbalance (Model XP105DR, Mettler Toledo) with a sensitivity of ±10 µg. The sampled filters were pre-equilibrated before weighing for at least 48 h in a conditioned room (20°C and 50% relative humidity).

The stations were selected with different designs chosen to obtain a wide range of PM sample characteristics (Table 1). They included a station with one wide tunnel with two rail tracks, separated by a middle wall in Joanic and Palau Reial stations and without middle wall in Santa Coloma, a single narrow tunnel with one rail track in Tetuan, a middle platform between two rail tracks in Sagrera and a single tunnel with one rail track separated from the platform by a glass wall with platform screen doors (PSDs) that are opened simultaneously with the train doors in Llefia. In two of these stations sampling was undertaken with only one ventilation setting, but measuring differences between days after night-time works and days under normal conditions to see if maintenance works in the tunnel

(addition of ballast or rail change) had any influences in the air quality of the platform the following day.

For the analysis of inorganic compounds one quarter of each filter was acid digested and subsequently analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) and Mass Spectrometry (ICPMS) to determine major and trace elements, respectively. A few milligrams of a standard reference material (NIST 1633a) were added to a fraction of a blank filter to check the accuracy of the analysis of the acid digestions. Another quarter of filter was water leached with deionized water to extract the soluble fraction and analysed by ion chromatography for determination of soluble anions, and by specific electrode for ammonium. A third portion of filter (1.5 cm^2) was used to measure total carbon (TC) using the Thermal Optical Transmittance (TOT) method by means of a laboratory OC-EC Sunset instrument. A detailed description of the analytical methodology is given by Querol et al. (2012) and Martins et al. (2016a). Blank filters were analysed in the batches of their respective filter samples and the corresponding blank concentrations were subtracted from each sample in order to calculate the ambient concentrations. Uncertainties were calculated as described by Escrig et al. (2009). The final quarter of the filter was then transferred to King's College London for Oxidative Potential analysis.

2.2. Processing of filters for toxicological assays

Four millimetre circle filter punches were carefully cut in triplicate from the supplied ¼ filter and placed directly into individual pre-labelled 1.5 mL micro-tubes (Simport Scientific, Canada). Care was taken to ensure the 4 mm Harris Unicore® puncher was kept clean (by rinsing with clean methanol after each punch) to avoid cross contamination by the $PM_{2.5}$ on the filters. A ratio was calculated (using πr^2) of the whole filter area (deposition area = 14733.7 mm^2) vs. the 4 mm filter punch area (area = 12.6 mm^2), and this was used to calculate the $PM_{2.5}$ mass deposited on the 4mm filter punch (Table S1). Considering both, the high loading of $PM_{2.5}$ (on the 4mm punch) and the possibly highly oxidizing nature of the $PM_{2.5}$, 1 mL of 200 µmoles L^{-1} of synthetic respiratory tract lining fluid (RTLF) containing equi-molar concentrations of ascorbic acid (AA), urate (UA) and reduced glutathione (GSH) was added to the tubes containing the 4mm filter punches and incubated for 4 hours at 37^{o}C with constant mixing. The final OP values discussed may therefore only be compared with the filters/$PM_{2.5}$ collected within this study or otherwise incubated under identical conditions.

In-house controls of particle-free, negative (M120, Cabot Corporation, USA) and positive (NIST1648a, urban particulate from NIST, USA) PM, and laboratory filter blanks, were incubated in parallel to the subway 4mm punched filters to control for background antioxidant oxidation, delivery of expected oxidation by the negative and positive controls in the RTLF exposure model, and for

checks of cross-contamination on lab filter blanks. To eliminate as much background antioxidant oxidation as possible from the model system, HPLC-grade water that had been treated previously with Chelex-100 resin (Sigma, UK) was used throughout for preparation of stocks and dilutions. Immediately following the 4 hour incubation the micro-tubes were centrifuged at 13,000 rpm for 1 hour at 4^{o}C, followed by removal of aliquots into 100 mM phosphate buffer pH7.5 (for GSH analysis) and 5% *meta*-phosphoric acid (for AA and UA analysis). All tubes were immediately stored at -70^{o}C.

2.3. Determination of Ascorbate, Urate and Glutathione

For the determination of AA and UA, this assay employs the technique of high performance liquid chromatography (HPLC, Gilson Scientific UK) with an electrochemical detector based on the method of Iriyama et al. (1984) with modifications. 50 µL of the centrifuged RTLF-exposed liquid was added to 450 µL of cold 5.6% *meta*-phosphoric acid in 0.7 ml amber HPLC vial. Aliquots of 20 µL acidified sample were injected onto a 150 x 4.6 mm 5µ SphereClone ODS(2) column (Phenomenex, UK) and eluted with a 0.2 mol L^{-1} K_2HPO_4-H_3PO_4 (pH 2.1) mobile phase containing 0.25 mmol L^{-1} octanesulfonic acid. Each sample/filter was prepared, exposed to the RTLF and analysed for GSH, AA and UA in triplicate. Each of these triplicates was injected only once in the HPLC to quantify AA and UA. Each individual standard was injected 3 times in the HPLC and the coefficient of variation was less than 5%, confirming the reproducibility of the method. Final concentrations for AA and UA were calculated with external AA/UA standards, which were run simultaneously with a Unipoint v5.1 software (Gilson Scientific UK). The %CV of analysis was less than 5% with a minimum detection limit for AA of 0.5 µmol L^{-1} and UA of 0.1µmol L^{-1}.

For the determination of GSH a spectrophotometric technique was used, measuring the absorbance of the diluted samples at 412nm (Gilson Instruments, UK). This assay employs the technique of the GSSG reductase-DTNB linked assay based on the method by Baker et al. (1990). 16.7 µL of the centrifuged RTLF-exposed liquid was added to 983.3 µL of cold 100 mM Sodium phosphate buffer pH7.5 containing 1 mM EDTA. 50 µL of this diluted sample was then analysed (in duplicate) in parallel with glutathione standards for both total glutathione (GSX) and (following derivatisation with 2-vinyl pyridine) for oxidised glutathione (GSSG). The reduced glutathione (GSH) was obtained by subtraction of the GSSG value from the GSX. The %CV of analysis was less than 10% with a minimum detection limit of 0.3 µmoles L^{-1}. The microplate reader used was a Spectramax190 (Molecular Devices, UK) along with the SoftMaxPro v4.8 software. All chemicals were of the highest grade possible, usually HPLC-grade, and purchased from either the Sigma Chemical Company (UK) or VWR (UK).

OP^{AA} and OP^{GSH} were used to indicate the oxidative potential represented by the capacity of PM to deplete AA and GSH. To obtain a metric for oxidative potential the data were expressed as

percentage depletion per µg of $PM_{2.5}$ (assuming a linear dose-function relationship, Ayres et al., 2008). The OP μg^{-1} $PM_{2.5}$ was next obtained by dividing the % antioxidant consumed (Table S2), by the $PM_{2.5}$ mass calculated to be present on the 4mm filter punch (Table S1) after being corrected for the background % oxidation observed for its relevant site field blank. Similarly to obtain an expression of the PM oxidative activity per m^3 of air we calculated the OP m^{-3} multiplying the OP μg^{-1} $PM_{2.5}$ by the concentration of $PM_{2.5}$ m^{-3} measured at the site during the $PM_{2.5}$ filter collection. The OP μg^{-1} $PM_{2.5}$ and the OP m^{-3} data for AA and GSH can also be combined together to provide a TOTAL oxidation potential value OP^{TOTAL} μg^{-1} $PM_{2.5}$, and OP^{TOTAL} m^{-3} respectively.

3. Results and Discussion

3.1. $PM_{2.5}$ subway chemistry

Average $PM_{2.5}$ masses for the samples selected are shown in Table 2. They ranged from 31 µg m^{-3} in Llefia during summer to 102 µg m^{-3} in Tetuan in winter and Palau Reial after night time works (addition of ballast). In general $PM_{2.5}$ concentrations were higher during the winter sampling period (with weaker ventilation settings, Martins et al., 2015). In the case of Sagrera the change of rails did not clearly affect the $PM_{2.5}$ concentrations, whereas the addition of ballast in Palau Reial did result in a clear increment. Chemical compositions of the subway $PM_{2.5}$ samples are provided on Table 3, based on averages of 6 samples per station (similar values are presented for average values for 30 days campaigns in Martins et al., 2016a; in agreement with the representativeness of the samples selected for this study). These results show high concentrations of Fe, Total Carbon (TC), Ba, Cu, Mn, Zn and Cr, all elements characteristic of the subway environment and sourced from rail tracks, wheels, catenaries, brake pads and pantographs. The great majority of subway particles are Fe-oxide (in the Barcelona subway mostly hematite formed by rapid oxidation of magnetite, Moreno et al., 2015), with Mn and Cr also sourcing from wheel and rail interactions. Carbon is the most important component of pantographs, brakes and motor brushes, the latter only being present in trains of Santa Coloma and Palau Reial lines. The trace elements Ba, Zn, Sb and Cu are also frequently present in notable concentrations and are attributed to brake abrasion, although their concentration depends on the type of brake. Thus Ba and Zn concentrations are higher in frontal brake pads (used in Santa Coloma and Palau Reial subway lines), whereas Sb and Cu are higher in lateral brake pads (used in Joanic, Tetuan and Llefia lines). Copper was especially high in the samples from Joanic, a station where the pantograph connecting to the electric supply catenary (which is made of 95% Cu wire for all lines) is made of copper or graphite (50% of trains each), whereas it is only graphite in the other subway lines (TMB own data). The best correlations (Pearson correlation coefficient) between chemical components for all stations were observed for silicate mineral-related elements (Al, Ca, K,

P, Li, Ti) which also showed strong correlation with some metals such as Co, Ni, Zn and Ba. Fe is correlated (R^2>0.8) with Co, As, Ti, Cr and Mn, whereas Cu is correlated with Sb (R^2=0.86).

PMF analyses have demonstrated that the mix of airborne particles varies from one station to another (Martins et al., 2016a), but that they can always be grouped broadly into outdoor and subway sources, the latter including all emissions generated by the circulation of trains (rail tracks, wheels, brake pads, catenaries and pantographs). The outdoor $PM_{2.5}$ sources include secondary particles (sulphate in summer and nitrate in winter) and a sea salt source identified by the presence of Na and Cl. A fourth source dominated by V was identified only for some stations and is suggested to represent fuel oil combustion, either from the effects of night maintenance works or, more likely, introduced from outside. The differences in the contribution of these sources between stations are attributed to the varying influence of outdoor air, which changes according to the time of the year, among other factors, and to the different design characteristics for each station.

3.2. Percentage of antioxidant consumed

Following measurement of the remaining antioxidants left in the 4h incubated RTLF, the data were initially corrected for the 4h particle-free control background oxidation (less than 5% loss) followed by a conversion to percentage antioxidants consumed with reference to the 4h particle-free (C4) control. With a starting concentration of 200 µmol L^{-1} antioxidant (C0) the remaining antioxidant concentrations after incubation of the in-house controls for 4h were as expected for the RTLF model used, with the negative control PM (M120) and the lab filter blank displaying no reactivity with the antioxidant (Fig. 1).

Among the three low-molecular-weight antioxidants (ascorbate AA, glutathione GSH and urate UA) in the synthetic RTLF, only AA and GSH were oxidized. As the consumption of UA was observed to be below 6% for all samples examined, it was considered not to be reacting with the $PM_{2.5}$ on the 4mm filter punch. Similar behaviour has been reported in other published works (Künzli et al., 2006; Sziget et al., 2014), hence UA will not be reported further. In the case of AA and GSH they were similarly consumed in the samples from Joanic, Tetuan and Llefia (4-6% difference), whereas at Santa Coloma, Sagrera and Palau Reial AA was clearly depleted in excess to that of GSH (a difference of 21-25%; Fig. 1 and Table S2 in supporting information). All controls and field blank filters show expected results reinforcing the accuracy of the assays results.

3.3. Assessment of oxidative potential

Both measurements of oxidative activity, that is ascorbate oxidation (expressed as OP^{AA} µg^{-1} or OP^{AA} m^{-3}) and glutathione oxidation (expressed as OP^{GSH} µg^{-1} or OP^{GSH} m^{-3}), showed considerable variation from station to station (Table 4). With regard to OP **per unit of mass**, the highest average

278 OP^{AA} (2.4 μg^{-1}), OP^{GSH} (1.9 μg^{-1}) and OP^{TOT} (4.3 μg^{-1}) values were obtained for Joanic station, whereas
279 the lowest average OP^{AA} (0.9 μg^{-1}), OP^{GSH} (0.4 μg^{-1}) and OP^{TOT} (1.3 μg^{-1}) values were registered at
280 Palau Reial. When looking at OP **per volume of air,** then Joanic again showed highest OP^{GSH} (98 m^{-3})
281 and OP^{TOT} (217 m^{-3}) values, as well as a high OP^{AA} value (119 m^{-3}), although in the latter case it was
282 very similar to that at Santa Coloma (123 m^{-3}). At the other extreme, although Palau Reial was again
283 low, the lowest overall OP measured in terms of volume was registered in the new "platform screen
284 door" station of Llefia where values were between three and six times less than those at Joanic
285 (Table 4).

286 Figure 2 includes samples collected from different times of the year, different platform depths
287 and designs, and (in the case of Sagrera and Palau Reial), samples collected before and after tunnel
288 night maintenance works. The OP data however, based on thirty-six samples, reveal no obvious
289 pattern linking these variables of season, design, and maintenance works with toxicity. It is
290 interesting to note that the new station of Llefia, fitted with platform screen doors, shows not only
291 low toxicity but the least variation between the two sampling periods (OP^{TOT} on Figure 2). This is
292 consistent with the fact that ventilation settings in these deep stations do not change much with the
293 season, producing a more stable atmospheric environment all year round. Similarly, the OP^{TOT} results
294 from Sagrera and Palau Reial reveal no influence of tunnel night works on platform PM toxicity.

295 The significance of associations between oxidative potential and PM chemical components was
296 assessed using the Spearman (ρ) rank order test, with a p-value <0.05 being considered to be
297 significant, and p<0.01 highly significant. In this test, which averaged the data for all thirty-six
298 samples assayed, OP values were highly significantly correlated for both AA and GSH when
299 considering both mass (ρ = 0.62) and volume (ρ = 0.77) (Table 5). When looking at OP^{AA} mass highest
300 correlations were obtained for Cd (ρ =0.50) and La (ρ =0.42), followed by Pb and Ce. In the case of
301 OP^{GSH}, Cu (ρ =0.64), Sb (ρ =0.50), La (ρ =0.48) and Ce (ρ =0.45) were all highly significantly correlated,
302 followed by P, Bi, As and Pb. In terms of volume the best correlations were obtained for Cu (ρ =0.35
303 OP^{AA}, ρ =0.53 OP^{GSH}), and significant correlations were revealed for Ba, As (OP^{AA}) and As (OP^{GSH}).
304 Therefore this analysis suggests there may be a link between both AA and GSH depletion and the
305 presence of certain trace metals.

306 Table 6 presents the averaged toxicological data for each station platform and compares metal
307 concentrations, highlighting highest levels in bold. These data demonstrate how, relative to the
308 other samples, Joanic $PM_{2.5}$ showed highest concentrations of Cu, Sb and La and Sagrera recorded
309 over double the Pb content of any other station. The Palau Reial samples had not just the highest
310 levels of $PM_{2.5}$ concentrations (due to high mineral dust content, as revealed by the enhanced Al
311 values), but also highest As, Sn, Zn, Fe, Cr and especially Ba. Given that the OP of the Palau Reial
312 samples is much lower than those from Tetuan, this leads us to conclude that Fe, Al, Ba, Cr, Sn and As

313 are not implicated as elements responsible for the oxidative potential of subway PM. In contrast, the
314 highest OP values coincide with notable enrichments in Cu and Sb (and, to a much lesser extent, La)
315 at Joanic.

316 Although other studies have reported only a weak association between OP^{AA} and OP^{GSH} in traffic-
317 related PM samples outdoors (Kelly et al., 2011), in the current study of samples collected
318 underground they were significantly correlated both in terms of mass and volume units. In the case
319 of the traffic-related PM samples Kelly et al. (2011) found strong correlations between Fe, Cu (both
320 redox-active metals, Buettner and Jurkiewicz, 1996), Ba, Mn, As, and Cd with both OP^{AA} and OP^{GSH}.
321 High correlations for OP^{AA} with Cu and Fe in PM have been reported in previous studies (Küenzli et
322 al., 2006; Godri et al., 2011), however studies using synthetic Fe-oxides including hematite (Fe_2O_3)
323 and magnetite (Fe_3O_4), have shown low or no toxicity (Kain, 2013) in agreement with these oxides
324 being thought to be relatively inert (Aust et al. 2002). CuO nanoparticles have also been reported to
325 generate high cytotoxicity and DNA damage (Karlsson et al., 2008b). Copper, together with Zn, Cr, Cd,
326 As and Pb, is a metal that can be affected by GSH binding (Davidson et al., 2015).

327 The correlation between OP and elemental composition can be influenced by many factors such
328 as the water solubility, chemical form, oxidation and reduction behaviour, capacity of ROS generation
329 or induction for example in Fenton-type, Haber–Weiss reactions, etc. (Szigeti et al., 2014). It has been
330 shown that the soluble fraction of metals such as Fe, Ni, and Cr plays a dominant role in ROS activity
331 (Kam et al., 2011b), and that metals in lower oxidation states can have a stronger oxidative effect
332 (Loxham et al., 2013). Particle size can also be a factor involved in the toxicity, previous works have
333 reported OP being greater in PM_{10} extracts than in $PM_{2.5}$ extracts (Kelly et al., 2011), with OP being
334 associated with elevated concentrations of metals such as Ba, Cu, Mo and Fe (linked to mechanical
335 wear on tires and brakes). However significant increases of these metals in larger size fractions did
336 not yield significant increases in OP^{AA} μg^{-1} in an experiment reported by Godri et al. (2011).

337 In the case of the Barcelona subway samples, our data suggest a possible link between OP (AA
338 and GSH) and some trace elemental concentrations, especially Cu, As and perhaps Sb. Copper
339 concentrations in these samples are related to the wear of brake pads and the electrical supply
340 (catenary and pantographs). In the case of Joanic, where Cu concentrations are highest, Cu is emitted
341 by the lateral brakes used by trains in subway line 4 (which are the richest in Cu of all four types of
342 brakes used in these subway trains), and the Cu pantographs that are still used in this line (although
343 it is being progressively changed to graphite as is the case with the rest of the lines). However other
344 metallic elements present in relatively high concentrations in the subway environment, such as Fe or
345 Cr, do not show correlation with OP values in any of the stations. In fact a highly significant negative
346 correlation was found with OP^{AA} μg^{-1} values, which would be consistent with the low oxidative

potential of hematite and magnetite, the most common iron compounds in the subway environment, as reported in the literature from other environments (Kain, 2013).

4. Conclusions

Our study of thirty-six samples from the Barcelona metro system considerably widens the database available on the toxicity of inhalable particles present on subway train platforms, and is backed-up by detailed chemical analyses. The main conclusions of this study are as follows:

- Of the three low-molecular-weight antioxidants in the synthetic RTLF, only AA and GSH were oxidised by subway $PM_{2.5}$ samples, with both indicators of oxidative activity presenting considerable variation between different subway platforms (ranges 0.9-2.4 OP^{AA} μg^{-1}; 0.4-1.9 OP^{GSH} μg^{-1}).
- The results indicate that the oxidative potential of subway PM samples is not obviously related to variations in $PM_{2.5}$ concentrations produced by changes in underground ventilation with the seasons, tunnel night works, or station design.
- Trace metals showing positive correlations between their concentrations and oxidative potential as measured by volume (OP^{AA} m^{-3} and/or OP^{GSH} m^{-3}) are identified as As, Mn, Zn, Ba and especially Cu. Copper is again implicated with regards to the OP^{GSH} μg^{-1} results, making it a possible trace metal contributor to subway particle oxidative potential, as has been suggested by several previous studies in different atmospheric environments (Kelly et al., 2011; Godri et al., 2011; Küenzli et al., 2006; Karlsson et al., 2008b; Kain, 2013).
- In our study the highest OP values coincided with PM samples containing notably enhanced levels of Cu and Sb, sourced from the wear of lateral train brakes and from Cu-pantographs.
- The assays employed in this study indicate that the strongly ferruginous component present in inhalable subway dust, despite its peculiar chemistry when compared to outdoor air, does not produce any obvious oxidative potential effect.
- Encouragingly, lowest OP^{TOT} m^{-3} values were found at the newest subway station, where the presence of platform screen doors coincides with improved air quality and reduced oxidative potential of ambient $PM_{2.5}$.

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Figures and Tables captions

Figure 1. Impact of antioxidant treatment on $PM_{2.5}$ induced AA and GSH depletion. Antioxidant remaining after 4 hour incubation for all filters. C0 beginning of the incubation period, C4 particle free control, M120 negative control, NIST1648a positive control. FB: field blank.

Figure 2. a) OP^{AA} μg^{-1} and the OP^{GSH} μg^{-1} $PM_{2.5}$, b) OP^{AA} m^{-3} and OP^{GSH} m^{-3}, c) OP^{TOTAL} μg^{-1} $PM_{2.5,}$ and OP^{TOTAL} m^{-3} for all collection dates and sites.

Table 1. Main information on the subway stations where air quality measurements were carried out.

Table 2: Average $PM_{2.5}$ concentrations ($\mu g\ m^{-3}$) for all filters collected at the 6 platforms, and also separating winter or summer time (with different ventilation protocol) and days after night maintenance works.

Table 3. Average chemical composition (and standard deviation in italics) of $PM_{2.5}$ samples collected at all sites under different ventilation systems (winter weaker, summer stronger) and after influence or not of night maintenance works. Higher values are highlighted in bold.

Table 4. Average OP values for AA and GSH on mass and volume basis.

Table 5. Spearman test values (ρ) for all variables considered. ** $p<0.01$, * $p<0.05$.

Table 6. Average OP total values on mass and volume basis, $PM_{2.5}$ concentrations, and concentrations of selected elements including those showing OP correlations (Cu to Ba, see Table 5), tracers of subway air particles (Fe, Cr from rail and wheels), and Al (tracer for addition of ballast during night-time works). $PM_{2.5}$, Fe and Al in $\mu g\ m^{-3}$, rest of elements in $ng\ m^{-3}$.

Supplementary information

Table S1: Calculation of $PM_{2.5}$ mass deposited on the 4mm filter punch used for toxicological assays.

Table S2. Percentage (and standard deviation) of antioxidant consumed, for ascorbate, urate and glutathione, during 4 hour incubation.

Table S3. Chemical composition of all $PM_{2.5}$ samples analysed in the six platforms.

Figure 1. Impact of antioxidant treatment on $PM_{2.5}$ induced AA and GSH depletion. Antioxidant remaining after 4 hour incubation for all filters. C0 beginning of the incubation period, C4 particle free control, M120 negative control, NIST1648a positive control. FB: field blank.

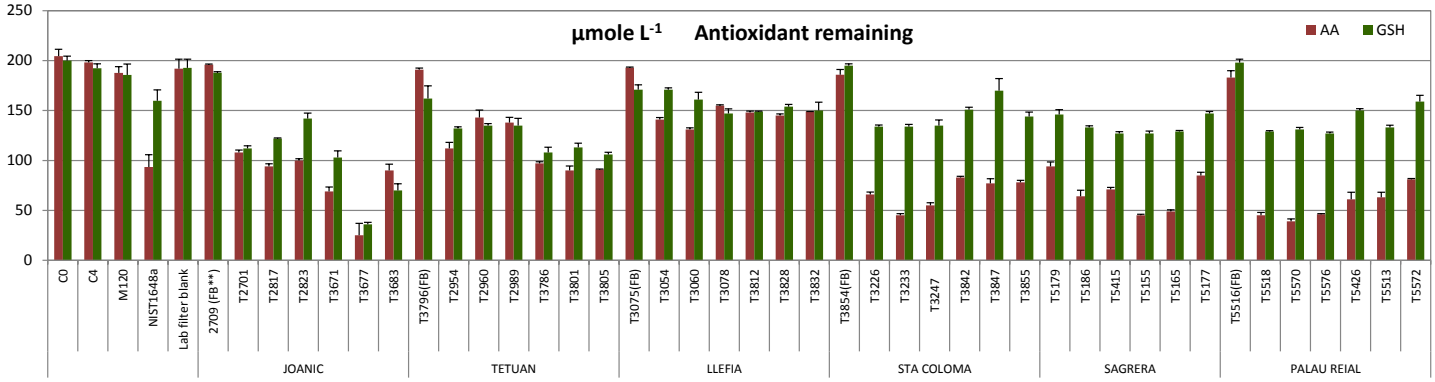
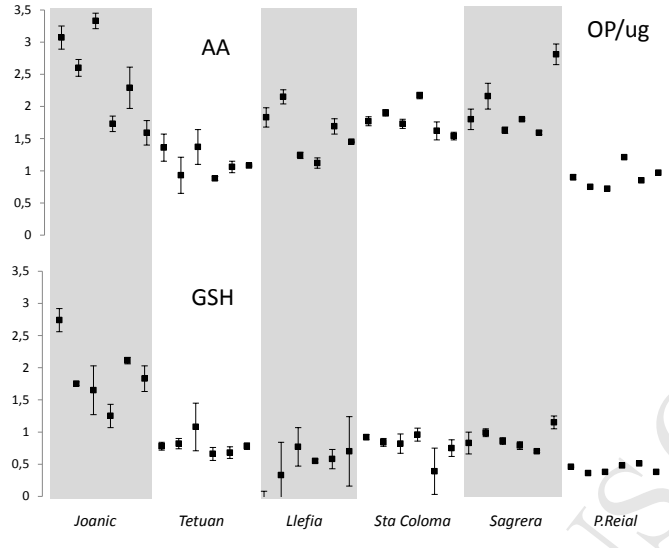
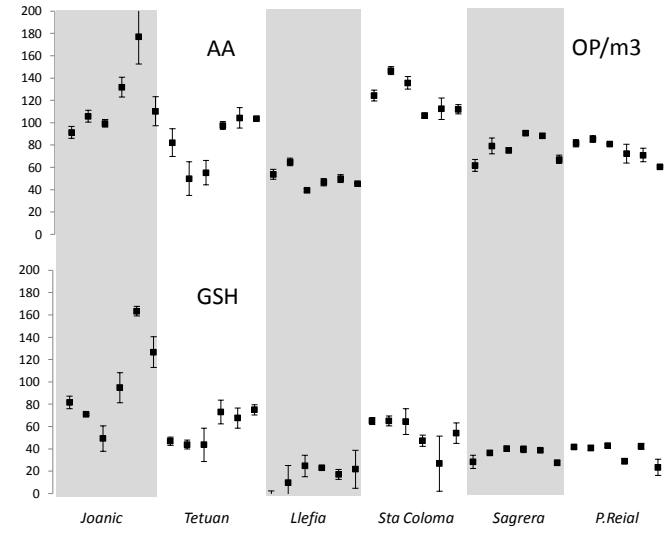


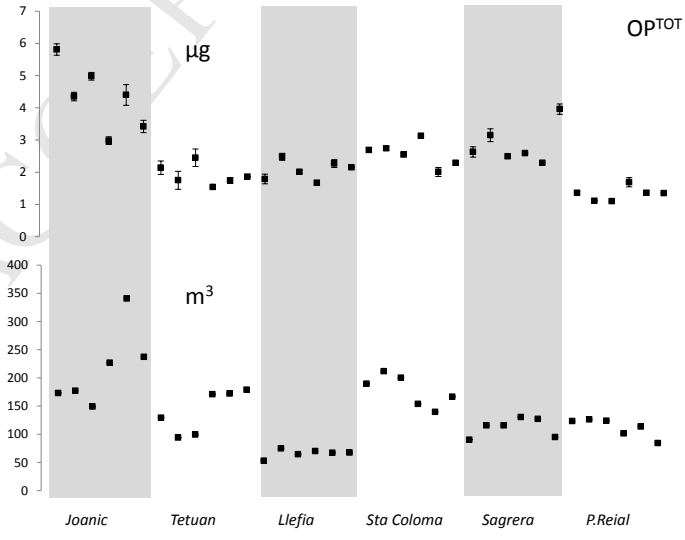
Figure 2. a) OP^{AA} μg^{-1} and the OP^{GSH} μg^{-1} $PM_{2.5}$, b) OP^{AA} m^{-3} and OP^{GSH} m^{-3}, c) OP^{TOTAL} μg^{-1} $PM_{2.5}$, and OP^{TOTAL} m^{-3} for all collection dates and sites.



a)



b)



c)

Table 1. Main information on the subway stations where air quality measurements were carried out.

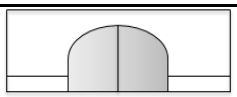
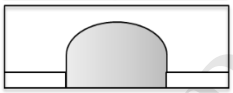
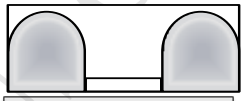
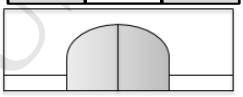
Subway station (line)	Variable measured	Depth (m)	Design
Joanic (L4)	winter/summer	-7.6	
Santa Coloma (L1)	winter/summer	-12.3	
Tetuan (L2)	winter/summer	-14.8	
Llefia (L10)	winter/summer	-43.6	
Sagrera (L5)	works/non-works	-10.5	
Palau Reial (L3)	works/non-works	-14.2	

Table 2: Average $PM_{2.5}$ concentrations (µg m^{-3}) for all filters collected at the 6 platforms, and also separating winter or summer time (with different ventilation protocol) and days after night maintenance works.

Station	average	summer	winter	works	non-works
Joanic	54	33	**74**		
Tetuan	77	51	**102**		
Llefia	33	31	34		
Sta Coloma	70	**75**	64		
Sagrera	41			39	43
Palau Reial	**87**			**102**	80

Table 3. Average chemical composition (and standard deviation in italics) of $PM_{2.5}$ samples collected at all sites under different ventilation systems (winter weaker, summer stronger) and after influence or not of night maintenance works. Higher values are highlighted in bold.

	Joanic		**Tetuan**		**Llefia**		**Sta Coloma**		**Sagrera**		**Palau Reial**	
μg m^{-3}	Averg.	σ	Averg.	σ	Averg.	σ	Averg.	σ	Averg.	σ	Averg.	σ
$PM_{2,5}$	54	*23*	77	*29*	32	*5*	70	*11*	41	*12*	**87**	*23*
Al	0,2	*0,1*	0,2	*0,2*	0,1	*<0,1*	0,3	*0,1*	0,3	*<0,1*	**0,8**	*0,5*
Ca	0,6	*0,3*	**1,3**	*0,9*	0,5	*0,2*	1,0	*0,3*	0,9	*0,3*	1,2	*0,5*
K	0,2	*0,1*	0,3	*0,2*	0,2	*0,1*	0,1	*0,1*	0,2	*0,1*	**0,3**	*0,2*
Na	0,2	*0,1*	0,3	*0,1*	0,1	*0,1*	0,1	*<0.1*	0,2	*0,1*	**0,4**	*0,2*
Mg	0,2	*0,1*	0,2	*0,1*	0,1	*<0,1*	0,4	*<0.1*	0,1	*<0,1*	**0,8**	*0,2*
Fe	19	*13*	29	*17*	8	*4*	17	*2*	12	*3*	**34**	*9*
SO_4^{2-}	1,3	*0,4*	**2,4**	*1,0*	0,9	*0,6*	2,1	*1,0*	1,3	*0,6*	2,3	*0,5*
NO_3^-	0,8	*0,2*	**1,7**	*1,4*	0,4	*0,1*	0,8	*0,4*	1,2	*0,9*	0,6	*0,1*
Cl^-	0,2	*0,1*	**0,5**	*0,2*	0,3	*0,3*	0,2	*0,1*	0,4	*0,2*	0,1	*0,2*
NH_4^+	0,3	*0,2*	**0,6**	*0,3*	0,2	*0,2*	0,5	*0,4*	0,4	*0,3*	0,5	*0,2*
TC	11	*3*	13	*5*	5	*2*	15	*7*	11	*3*	**16**	*4*
ng m^{-3}												
P	24	*9*	30	*18*	10	*6*	24	*4*	**35**	*7*	31	*10*
Li	0,3	*0,1*	0,4	*0,2*	0,2	*0,1*	0,4	*0,1*	0,5	*0,2*	**1,0**	*0,3*
V	4	*2*	**8**	*7*	4	*2*	6	*2*	2	*2*	5	*2*
Co	1,2	*0,8*	1,3	*0,6*	0,4	*0,1*	1,0	*0,2*	1,0	*0,2*	**2,4**	*0,4*
Ni	8	*3*	8	*2*	4	*1*	9	*1*	8	*2*	**24**	*5*
As	1,7	*0,9*	1,6	*0,8*	0,6	*0,3*	1,3	*0,3*	1,1	*0,6*	**2,1**	*0,5*
Se	0,3	*0,1*	0,3	*0,1*	0,3	*0,1*	0,3	*0,1*	0,2	*0,1*	0,4	*0,0*
Rb	0,6	*0,2*	0,9	*0,6*	0,4	*0,2*	0,5	*0,2*	0,5	*0,1*	**1,2**	*0,7*
Sr	3	*1*	6	*4*	2	*14*	17	*3*	4	*1*	**50**	*11*
Zr	9	*1*	13	*4*	11	*4*	8	*3*	16	*0,4*	**21**	*3*
Mo	20	*5*	8	*4*	16	*8*	20	*2*	13	*2*	**31**	*14*
Cd	0,2	*<0.1*	0,2	*0,1*	0,1	*0,1*	0,2	*0,1*	0,3	*0,1*	0,2	*0,1*
Sn	7	*3*	8	*4*	3	*0,7*	7	*2*	**10**	*4*	**11**	*2*
Sb	**72**	*35*	28	*16*	9	*6*	3	*1*	6	*1*	3	*0,4*
La	**0,6**	*0,1*	0,4	*0,2*	0,2	*<0,1*	0,3	*0,1*	**0,6**	*0,1*	**0,6**	*0,1*
Ce	**1,1**	*0,2*	0,9	*0,4*	0,3	*0,1*	0,7	*0,2*	**1,3**	*0,3*	**1,1**	*0,3*
Pb	10	*2*	8	*3*	5	*3*	10	*6*	**26**	*11*	10	*2*
Bi	0,4	*0,3*	0,4	*0,2*	0,3	*0,2*	0,4	*0,5*	0,4	*0,2*	0,2	*0,1*
Th	0,1	*0,1*	**0,2**	*0,1*	0,1	*0,1*	0,1	*<0.1*	0,1	*<0.1*	0,1	*0,1*
U	0,2	*0,1*	0,2	*0,1*	0,1	*0,1*	0,1	*<0.1*	0,1	*<0.1*	<0,1	*<0,1*
Ti	18	*8*	21	*14*	7	*3*	25	*7*	19	*7*	**43**	*18*
Cr	25	*17*	36	*21*	13	*6*	18	*5*	13	*2,9*	42	*8*
Mn	187	*131*	**288**	*176*	79	*37*	165	*42*	107	*27*	**301**	*74*
Cu	**331**	*251*	177	*97*	33	*12*	105	*18*	131	*25*	188	*45*
Zn	193	*78*	137	*66*	56	*30*	172	*50*	104	*14*	**318**	*8*
Ba	102	*55*	55	*32*	13	*8*	732	*182*	103	*15*	**1980**	*496*

Table 4. Average OP values for AA and GSH on mass and volume basis.

	$OP^{AA}\mu g^{-1}$	$OP^{GSH}\mu g^{-1}$	$OP^{AA}m^{-3}$	$OP^{GSH}m^{-3}$	$OP^{TOT}\mu g^{-1}$	$OP^{TOT}m^{-3}$
Joanic	**2,4**	**1,9**	**119**	**98**	**4,3**	**217**
Tetuan	1,1	0,8	82	58	1,9	141
Llefia	1,6	0,5	50	16	2,1	66
Sta Coloma	1,8	0,8	**123**	54	2,6	177
Sagrera	2,0	0,9	77	35	2,9	112
Palau Reial	0,9	0,4	75	37	1,3	112
M120	0,1	0,1			0,2	
NIST1648a	1,1	0,3			1,4	

Table 5. Spearman test values (ρ) for all variables considered. ** p<0.01, * p<0.05. PM chemical species are expressed in μg g^{-1} in all cases.

	$OP^{AA}\mu g^{-1}$	$OP^{GSH}\mu g^{-1}$	$OP^{AA}m^{-3}$	$OP^{GSH}m^{-3}$
OP^{GSH} μg^{-1}	0,62**			
OP^{GSH} m^{-3}			0,77**	
$PM_{2,5}$	-0,61**	-0,24**	0,54**	0,52**
Al	-0,04	-0,15	0,00	-0,23
Ca	-0,10	-0,07	-0,29	-0,32
K	-0,16	-0,19	-0,29	-0,27
Na	0,14	0,10	-0,29	-0,31
Mg	-0,44*	-0,50**	0,05	-0,15
Fe	-0,56**	-0,14	0,07	0,25
SO_4^{2-}	-0,03	-0,29	-0,01	-0,09
ws-NO_3^-	0,06	0,07	-0,01	0,01
ws-Cl^-	-0,01	0,05	-0,46**	-0,32*
ws-NH_4^+	0,22	-0,06	0,09	-0,01
P	0,30	0,40*	0,11	0,10
Li	-0,19	-0,14	-0,17	-0,20
V	0,16	-0,04	0,04	-0,07
Co	-0,23	0,01	0,10	0,11
Ni	-0,05	-0,12	-0.08	-0,15
As	0,12	0,36*	0,35*	0,40*
Se	0,04	0,23	-0,30	-0,28
Rb	-0,15	-0,07	-0,24	-0,12
Sr	-0,38*	-0,28	0,19	-0,01
Mo	0,18	0,25	-0.25	-0,19
Cd	0,50*	0,26	-0,16	-0,19
Sn	0,23	0,25	0,05	0,01
Sb	0,27	0,50**	-0,03	0,33
La	0,42*	0,48**	0,12	0,13
Ce	0,37*	0,45**	0,08	0,08
Pb	0,40*	0,34*	-0,11	-0,13
Bi	0,28	0,37*	-0,14	-0,02
Ti	-0,16	-0,07	0,18	0,04
Cr	-0,54**	-0,16	-0,12	0,15
Mn	-0,51**	-0,09	0,12	0,30
Cu	0,29	0,64**	0,35*	0,53**
Zn	0,05	0,21	0,20	0,22
Ba	-0,15	-0,08	0,37*	0,14
TC	0,25	0,23	0,09	-0,06
PMF sources				
Subway	-0,28	0,12	0,20	0,44*
Secondary	0,40*	-0,36	0,09	-0,43*
Sea salt	0,08	0,48*	0,19	0,27
Oil combustion	-0,02	-0,02	-0,34	-0,62*

Table 6. Average OP total values on mass and volume basis, $PM_{2.5}$ concentrations, and concentrations of selected elements including those showing OP correlations (Cu to Ba, see Table 5), tracers of subway air particles (Fe, Cr from rail and wheels), and Al (tracer for addition of ballast during night-time works). $PM_{2.5}$, Fe and Al in μg m^{-3}, rest of elements in ng m^{-3}.

	OP^{TOT} μg^{-1}	OP^{TOT} m^{-3}	$PM_{2.5}$	Cu	As	La	Cd	Sb	Sn	Pb	Zn	Ba	Fe	Cr	Al
Joanic	**4,3**	**217**	54	**331**	1,7	**0,6**	0,2	**72**	7	10	193	102	19	25	0,2
Tetuan	1,9	141	77	177	1,6	0,4	0,2	28	8	8	137	55	29	**36**	0,2
Llefia	2,1	66	33	33	0,6	0,2	0,1	9	3	5	56	13	8	13	0,1
Sta Coloma	2,6	177	70	105	1,3	0,3	0,2	2	7	10	172	732	17	18	0,3
Sagrera	2,9	112	41	131	1,1	0,6	0,3	6	10	**26**	104	103	12	13	0,3
Palau Reial	1,3	112	**87**	188	**2,1**	0,6	0,2	3	**11**	10	**318**	**1980**	**34**	**42**	**0,8**

Oxidative Potential of Subway $PM_{2.5}$

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Highlights

- Oxidative activity shows considerable variation between different subway platforms
- Subway PM oxidative potential is not linked to ventilation or tunnel night works
- Highest oxidative potential coincide with PM with higher levels of Cu, As and Sb
- The strongly Fe component in PM subway does not produce any obvious toxic effect
- Lowest oxidative stress was found at station with PSDs